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15. Supplementary Notes

16. Abstract (Limit: 200 words)

This progress report describes the initial favorable results of what probably will become a viable method for the deposition of cubic BN on silicon substrate. During this study, energy fluence of laser beam and the target material (type, form, purity etc) were identified to be the two most critical parameters. In the past month, we have attempted two procedures to synthesize cubic BN: dual-beam laser ablation of a high purity, sintered hexagonal BN (HBC grade from Union Carbide), and single-beam laser ablation of a high purity, CVD grown pyrolytic BN. Raman and IR spectroscopy as well as X ray diffraction analysis of films indicated some evidence of cubic BN. Additional work is to be done in order to optimize the procedure such that only cubic form of BN will be grown.

17. Document Analysis a. Descriptors

b. Identifiers/Open-Ended Terms: Thin Films, Electronics, Laser, Ablation

c. COSATI Field/Group

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SBIR Phase I Research Progress Report # 3

Introduction

In progress reports # 1 and # 2, the results of an excimer (248 nm, KrF) laser ablation of sintered, high purity hexagonal BN (HBC grade from Union Carbide) were presented. The films obtained on Si <100> were mostly amorphous with no evidence of cubic form of BN. In addition, a large number of micron-sized particles and loosely adherent films were observed. Experiments as a function of energy fluence showed high growth rates and increased particulate density with increasing energy fluence.

We believe that the inability to obtain cubic BN and to minimize particulates is due to two factors: the characteristics of target and the pulse energy fluence. Although purity was satisfactory, the HBC grade target was flaky in nature and had a strong tendency to disintegrate into particles due to thermal stresses caused by the laser beam. In laser ablation, an important requirement is the production of energetic ionized and excited species (10-100 eV) with high velocities (10^6-10^7 cm/sec) and thereby promote film crystallinity and dense packing. In order to achieve these conditions, dense and pure target, and high pulse energy fluence are essential.

During this report period, we have ordered and received an improved target namely pyrolytic BN (pBN) from Union Carbide Advanced Ceramics section. It took four weeks to receive this target. While waiting for pBN target, we have attempted a dual-beam approach namely simultaneous ablation of HBC grade target with excimer and Nd:YAG laser beams. The objective was to increase the velocity and energy of ablated species needed to create cubic BN. The rationale for the dual-beam approach is based upon Mineta et al's work [1] who used a hybrid technique combining a continuous wave, high power CO_2 laser and an ion beam technique to produce cBN films. Essentially, the CO_2 laser was used to evaporate the target while the the ion source caused the ionization of nitrogen which subsequently imparted high energy to the film causing the conversion from hexagonal to cubic.

In addition to dual-beam method, preliminary experiments with single beam, excimer laser ablation of pBN were performed.

Experiments and Results

1. Dual-Beam Ablation of HBC Grade Target

The experimental arrangement for the dual-beam pulsed ablation technique is illustrated in Figure 1. A photograph of the experimental setup is also shown in Figure 2. This is similar to the single-beam ablation of the target described in progress report # 1. A six-way vacuum chamber with provisions for substrate preheating, mounting of the target and windows for the laser beams was used. The vacuum chamber was evacuated $< 10^{-7}$ torr using mechanical and diffusion pumps. The substrate was Si<100>, etched thoroughly in 49% HF acid for 10 minutes and then preheated to 500°C. The target was mounted at about 20 mm from the substrate and was rotated at 50 rpm using an external magentic device-motor arrangement.

A pulsed excimer laser and a pulsed Nd:YAG laser, the specifications of which are given in Table 1, were used. First, the Nd:YAG beam was impinged on the target leading to melting or evaporation of the target. Once the target was in molten or evaporation state, a pulsed excimer beam was used to irradiate the target causing ablation. The consecutive interactions of Nd:YAG and excimer lasers on BN target is expected to aid in reducing the particles as well as increasing the kinetic energies of species as they arrive at the substrate surface.

Table 1. Laser Specifications

Laser type	Excimer	Nd:YAG
Wavelength, nm	248	1064
Pulse energy, J max.	0.4	1
Pulse width, nsec	10-20	150,000
Repetition rate, Hz	1-100	1-20
Energy fluence, J/cm^2	3-5	1-10

After deposition, the substrate was allowed to cool to ambient temperature. Film quality was studied using X ray diffraction, Raman and IR spectroscopy.

The laser parameters with the dual beam method are given below.

		Sample # 12	Sample # 14
Nd:YAG	Pulse energy, J	3	0.65
	Pulse rate, Hz	1	10
Excimer	Pulse energy, J	0.4	0.4
	Pulse rate, Hz	1	10
Deposition time, min.		45	20

Visual examination and SEM analysis (along with wavelength X-ray dispersive spectrometry) of films on samples 12 and 14 indicated the presence of thin films of BN, the thickness being larger in sample 14 as compared to sample 12. Further, the film in sample 12 contained few particles as compared to sample 14. Figure 3 shows the presence of micron-sized particles in sample 14. Particulate density is attributed to higher energy density and the sintered HBN target. X-ray diffraction data using copper K alpha radiation (wavelength = 1.5418 A) of samples 12 and 14 are given in Figures 4 and 5. It can be seen that sample 14 exhibited a strong peak corresponding to cubic BN <111> plane while sample 12 did not show CBN peak. This may be due to the thinness of film in sample 12. There are also additional peaks in X ray patterns which were identified to be boron. Several peaks around 50^{o} to 60^{o} are difficult to be identified inspite of a computer search with compounds of B, N, Si and O_2. It should be added that the sharpness of peak for CBN indicates a high degree of crystallinity. MicroRaman spectroscopy of sample 14 revealed the presence of CBN (Figure 6). However, IR spectroscopy did not clearly provide sp^3 bonding characteristic of CBN and may be explained to be due to the nitrogen deficiency in BN (Figures 7 and 8).

It should be emphasized that single-beam excimer ablation of HBN target (Reports 1 and 2), in contrast to dual-beam ablation, did not yield any indication of the formation of CBN. There is a significant potential in dual beam approach with pBN target.

2. Single-Beam Excimer Ablation of pBN Target

Since purity, density and crystalline form of BN target material play vital roles in determining the film formation, the pyrolytic BN as a target source was attempted. pBN is an extremely pure material with a laminar type of structure. pBN is produced by a patented chemical vapor deposition process on a high purity graphite rod. pBN has improved density, thermal shock resistance, oxidation resistance, outgassing, and porosity over the HBC grade (see the manufacturer's specifications for pBN in Appendix). In this work, we have used pBN target (0.8 mm thickness on a 12 mm diameter graphite rod) for single-beam excimer ablation.

Since the target was received a week before this report's due date, we have conducted only one experiment but repeated several times (samples 16 through 19). The experimental conditions were: pulse energy = 270 mJ, pulse rate = 10 Hz, Other parameters remained same as described before. Visual and SEM examination of samples indicated strongly adherent films with very few particulates especially when compared with the films deposited from the HBC grade. An SEM micrograph of film is shown in Figure 9.

The analysis of these films were limited to only IR spectroscopy. X ray and Raman analysis will be done later. IR spectrums do show some evidence of sp^3 bonding at 1090 cm^{-1} characteristic of CBN (Figures 10 and 11).

Discussion

The unique features of pulsed laser ablation are: generation of high energy particles from the coupling of large optical field with soild targets. For a 248 nm excimer laser, neutral atoms, ions and molecules in the energy range 2 eV to 850 eV can be generated at pulse laser energy fluences of upto 10 J/cm^2 [2]. The energy distribution of these particles largely depend upon both on the absorption charcteristics of the target and the plasma produced. We shall discuss the implications of dual-beam laser technique.

For a solid BN target, the threshold value for a 248 nm KrF excimer laser is experimentally determined to be 0.31 to 0.34 J/cm^2 [3]. The laser fluence using our excimer laser and a 100 mm focal length lens can be as high as 5 J/cm^2. Thus ablative photodecomposition can easily occur even in solid BN and the ablated material is removed layer by layer on a pulse per pulse basis. But by prior melting or evaporating the BN target with the YAG beam, the ablation rate by the excimer beam and the energies of ablated species can be substantially increased because of the increased free carrier concentration. Liquid or gaseous sources have enhanced absorption due to radiation trapping and develop high temperatures due to low thermal conductivity. Excimer laser ablation immediately following the YAG beam melting will result in high absorption by the target which in turn tends to produce large number of ions in preference to neutrals. In addition, the velocity of the ablation front (v) given by the expression, $v = I/p\,H_s$ where I = absorbed laser power density, p = density, H_s = heat of sublimation, will be considerably higher resulting in congruent ablation. High energy species can break atomic bonds, cause thermal spikes, generate subsurface vacancies, enhance adsorbed atom mobility, and generate nucleation centers which are similar to ion beam deposition [4].

In pulsed laser ablation, the most significant problem is the deposition of particles of the order of 0.1 to 10 microns size. The particles are basically solidfied droplets and granular materials due to the fracture of target. Energy fluence and physical properties of the target largely determine the particulate formation. In the work, the use of dual-beam should reduce the particles. For example, the use of liquid germanium as a target resulted in virtual elimination of particulates [4]. In addition, the dual beams heating of the target will produce colliding vapor plumes that will generate high pressure sufficient to break the particles. Although we have not observed any drastic reduction in particulate density in dual-beam approach, we believe that the HBC grade source was the major cause of particles. The use of pBN largely reduced the presence of particulates and substantially improved the adherence over the HBC grade. In addition, there is some evidence of CBN when pBN target was used even with a single-beam.

Summary and Future Work

The work performed so far indicates some positive signs of CBN synthesis with laser ablation technique. Continued experiments are necessary to confirm the presence of CBN. A critical factor is the type of target that determines the growth and characteristics (adherence, particles etc) of CBN. Initial experiments showed that pBN source is superior than HBC grade. We shall continue to experiment with pBN target both in single and dual beam modes.

We also attempt to use CBN target which may even be superior than pBN. For obtaining CBN target, we have contacted GE Superabrasives Division and found the availability of a high purity CBN insert (experimental grade BZN 6000). Future work will involve pBN and CBN targets.

Bibliography

1. S. Mineta et al, Thin Solid Films, 189, 1990, 125
2. D.C. Paine and J.C. Bravman (eds.), Laser Ablation for Materials Synthesis, Materials Research Society, Vol. 191, 1990
3. G.L. Doll et al, in Reference 2, 55
4. H. Sankur and J.T. Cheung, Applied Physics A, 47, 1988, 271

APPENDIX

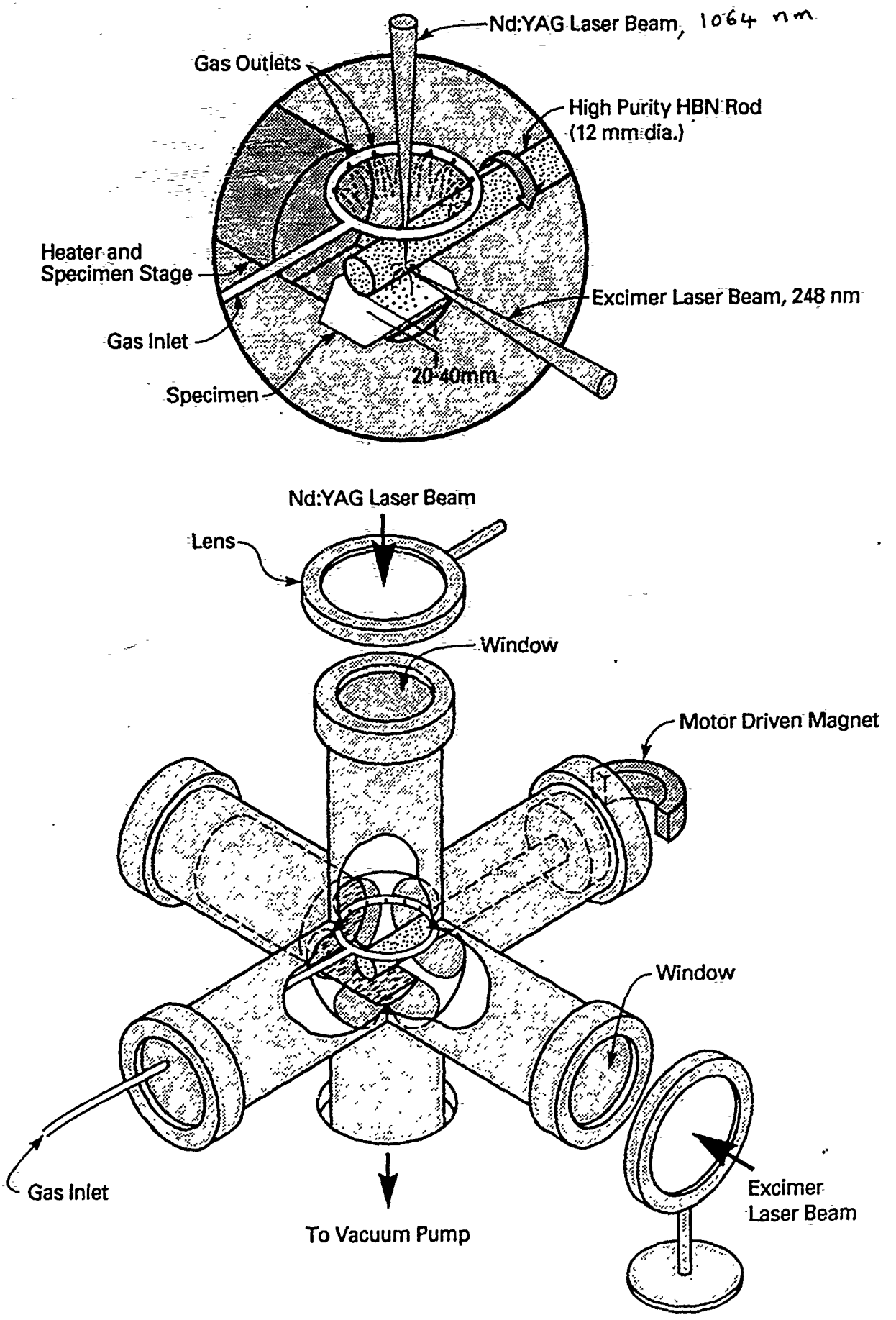


Figure 1. Schematic of Dual-Beam Ablation Method

Figure 2. A photograph of dual-beam experiment

A Excimer Laser

B Nd:YAG Laser

C Vacuum Chamber

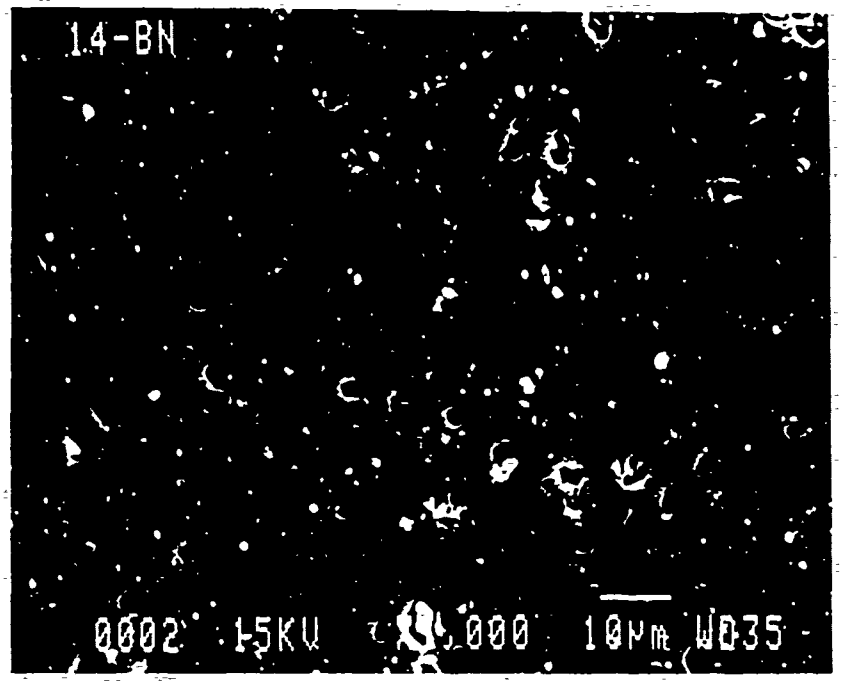


Figure 3. SEM micrograph of sample # 14 showing large number of particles

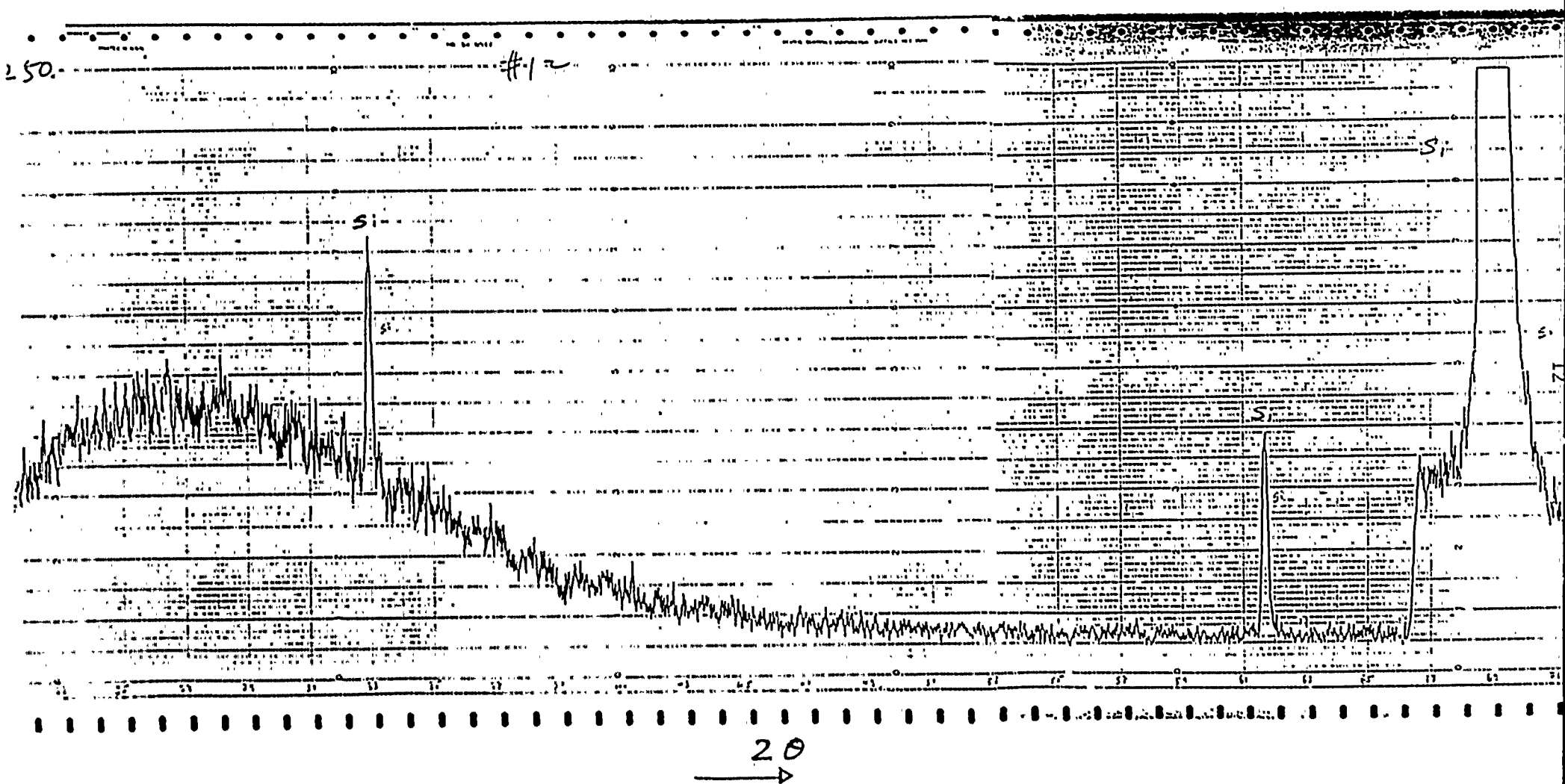


Figure 4. X-ray diffraction pattern of sample # 12

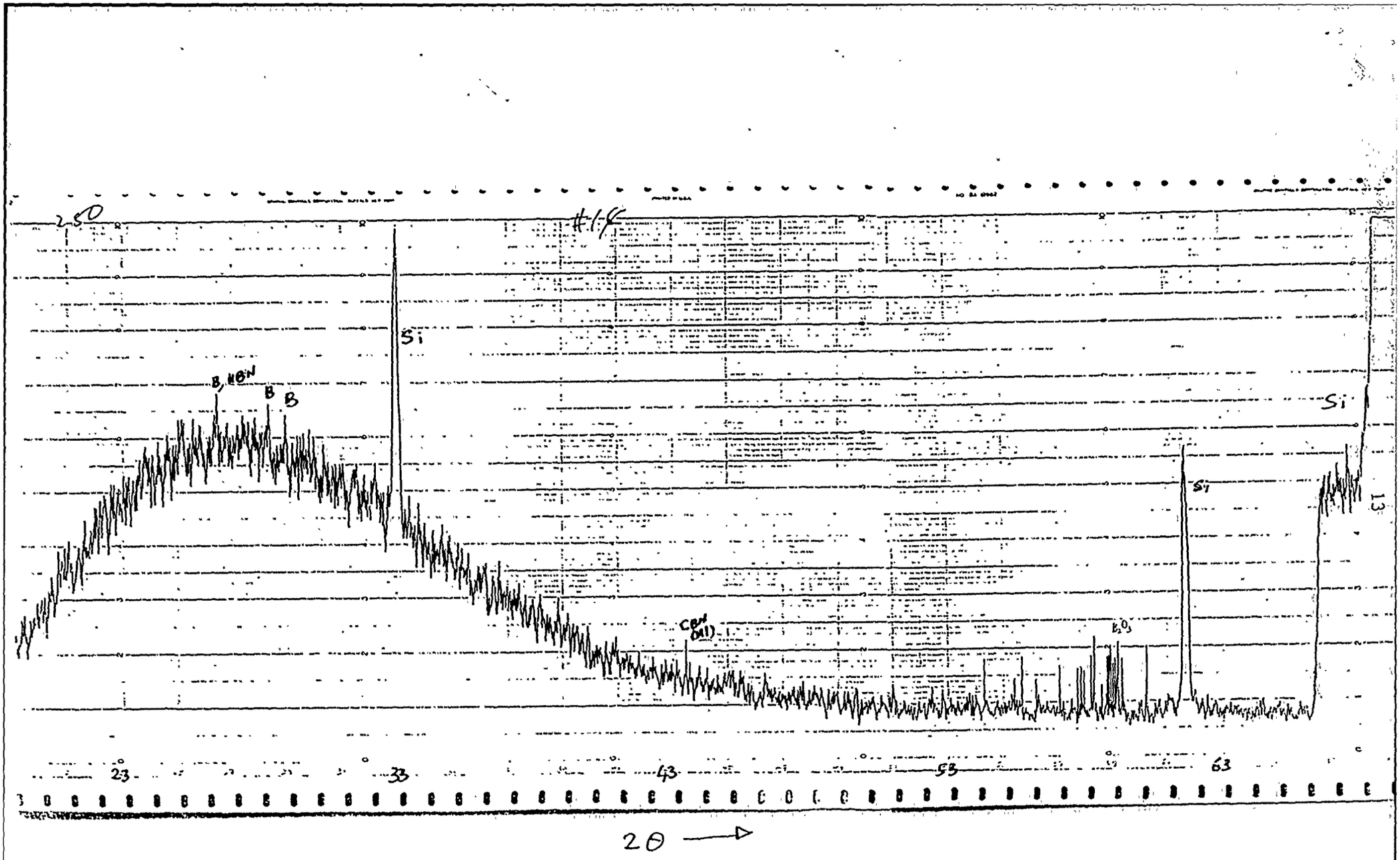


Figure 5. X-ray diffraction pattern of sample # 14

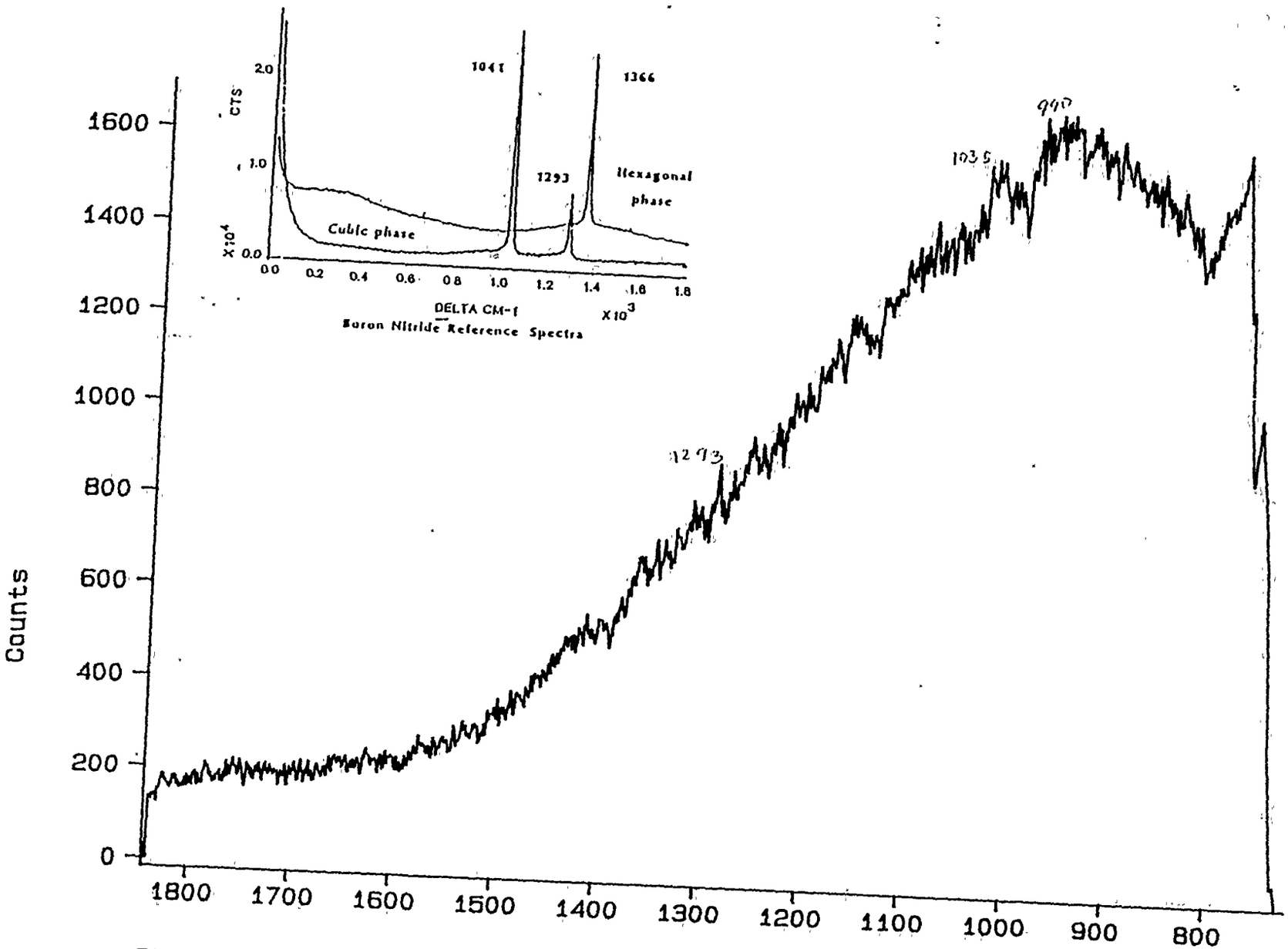
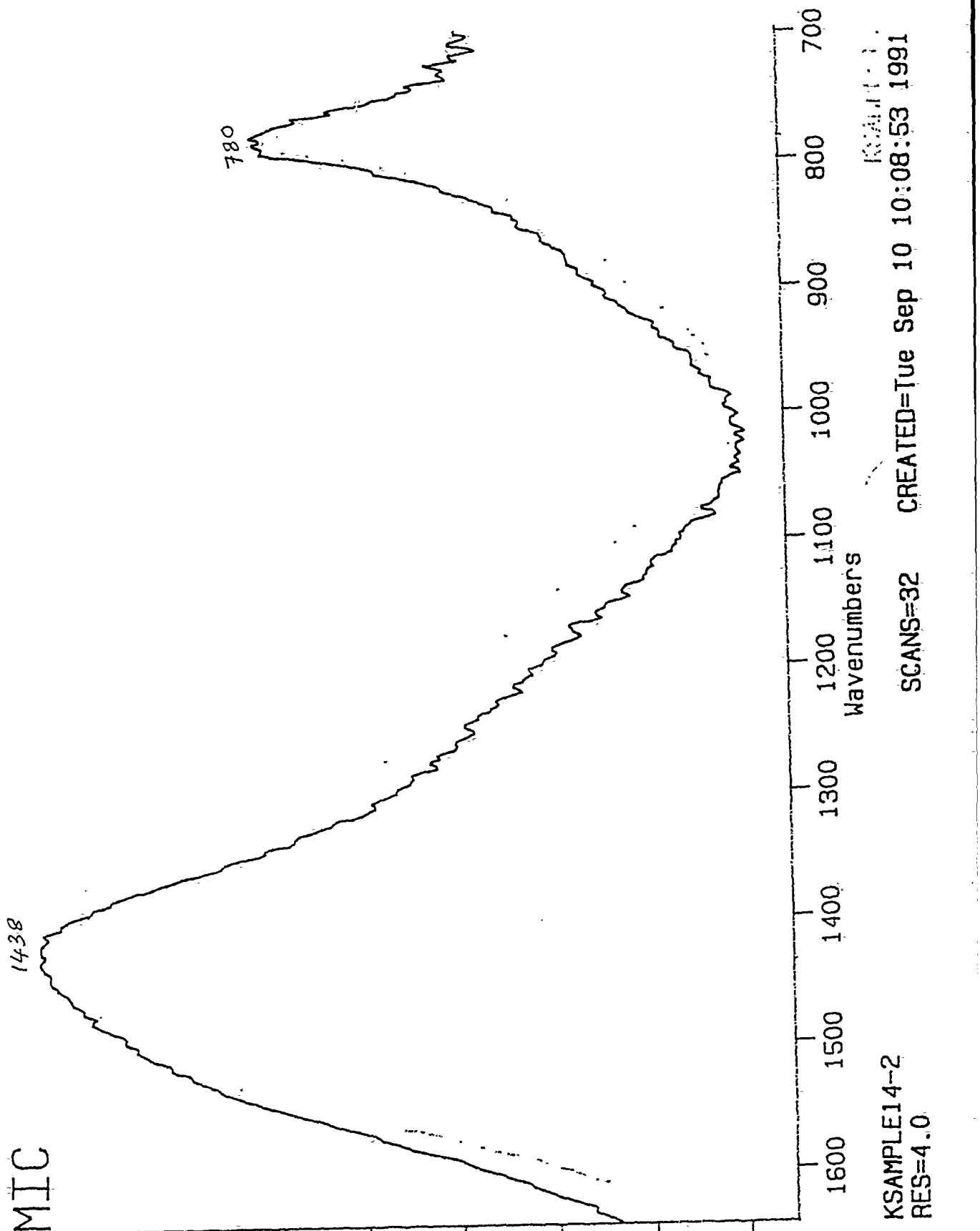


Figure 6. Raman spectrum of sample # 14

F14.dat
6/18/91

Figure 7. Infrared Spectrum of Sample # 14 at two locations



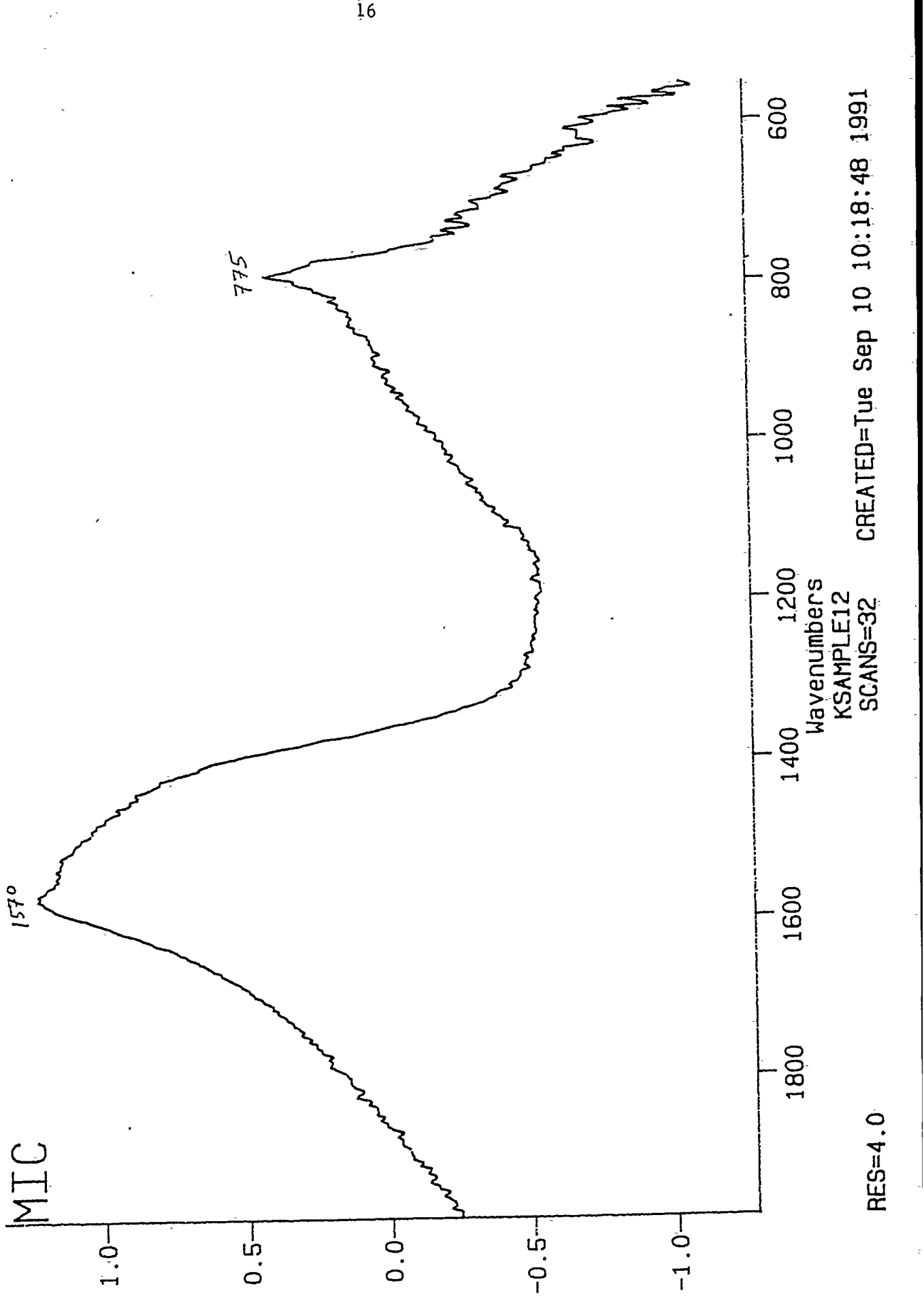


Figure 8. Infrared Spectrum of Sample # 12

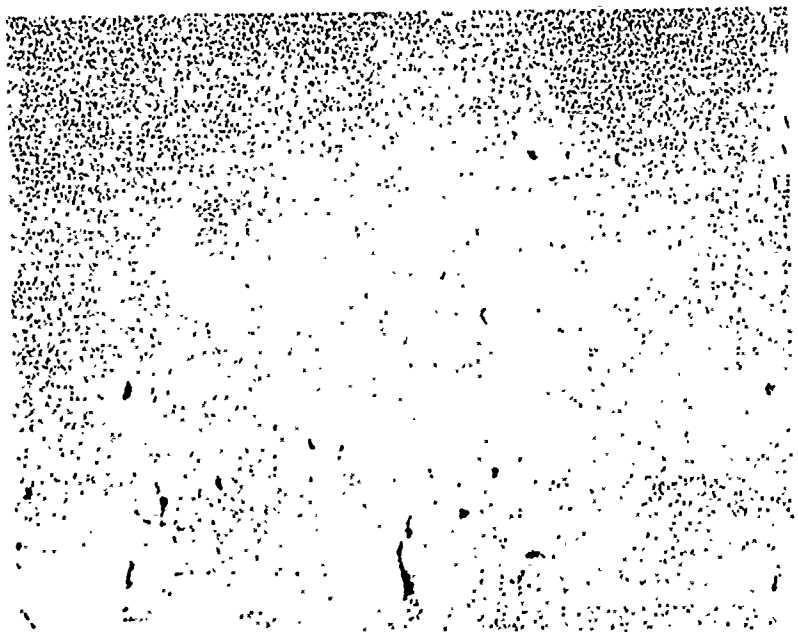


Figure 9. SEM micrograph of sample # 16 showing few particles

Figure 10. Infrared Spectrum of Sample # 18

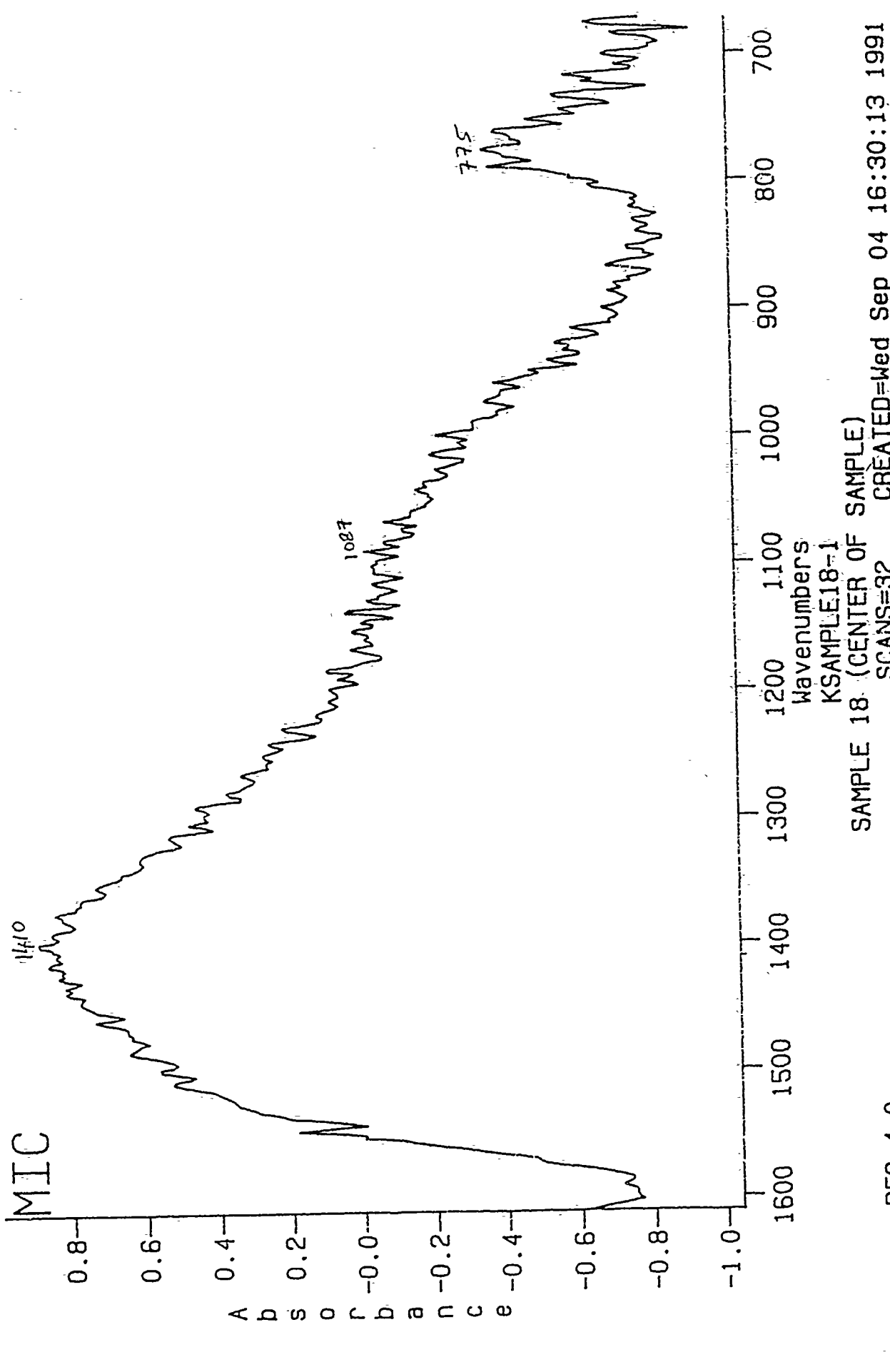
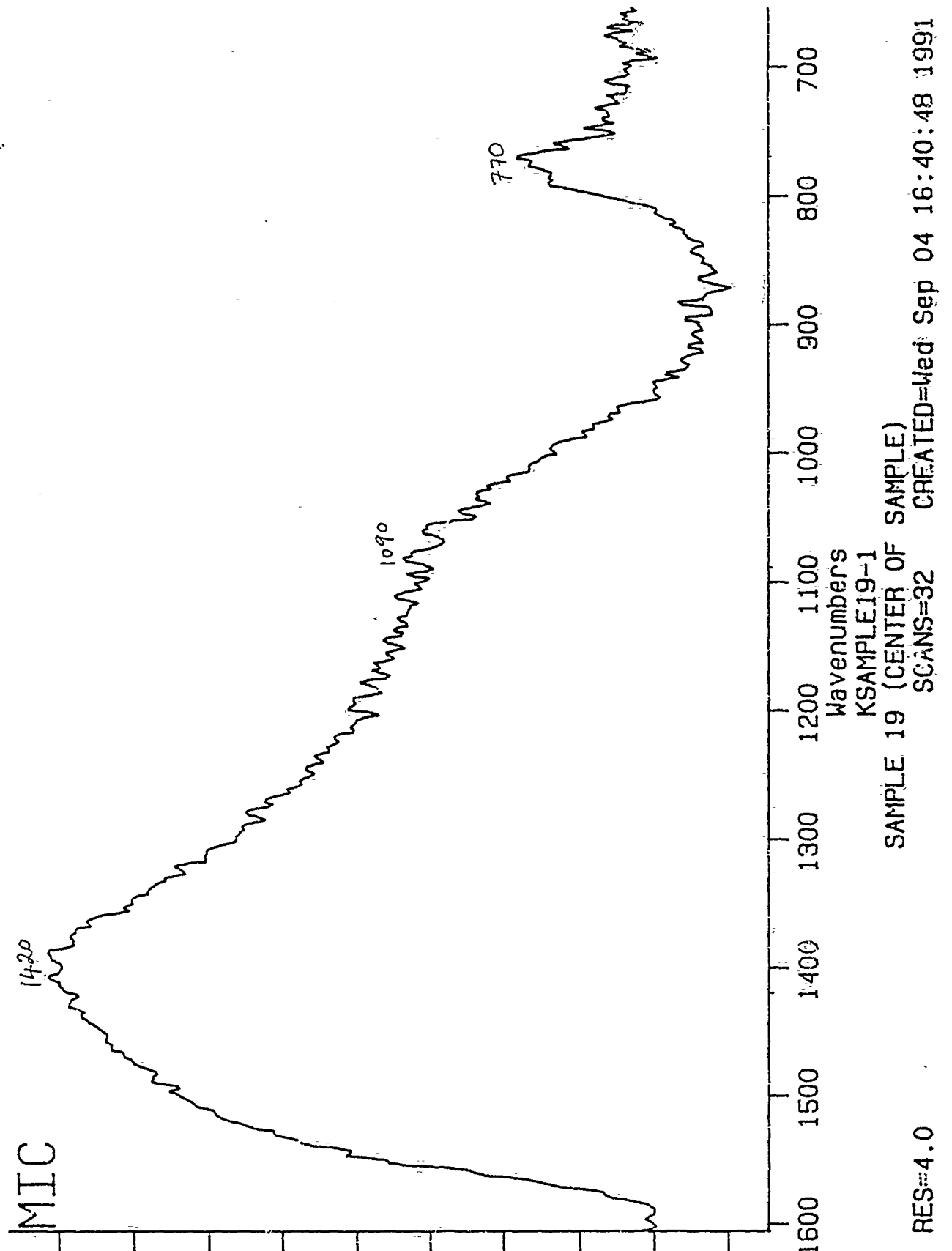


Figure 11. Infrared Spectrum of Sample # 19



PROPERTIES OF PYROLYTIC BORON NITRIDE (DATA FROM UNION CARBIDE)

TYPICAL PROPERTIES

Typical Spectroscopic Analysis of "BORALLOY" Pyrolytic Boron Nitride

Element	*Results*	*Element*	*Results*
Ag	ND	Mo	ND
Al	ND	Na	ND
As	ND	Nb	ND
Au	ND	Nd	ND
B	H	Ni	ND
Ba	ND	Os	ND
Be	ND	Pb	ND
Bi	ND	Pd	ND
Ca	VVFT	Pr	ND
Cd	ND	Pt	ND
Ce	ND	Rb	ND
Co	ND	Re	ND
Cr	ND	Rh	ND
Cs	ND	Ru	ND
Cu	VVFT	Sb	ND
Dy	ND	Si	VVFT
Er	ND	Sm	ND
Eu	ND	Sn	ND
Fe	ND	Sr	ND
Ga	ND	Ta	ND
Gd	ND	Tb	ND
Ge	ND	Te	ND
Hf	ND	Th	ND
Hg	ND	Ti	ND
Ho	ND	Tl	ND
In	ND	Tm	ND
Ir	ND	U	ND
K	ND	V	ND
La	ND	W	ND
Li	ND	Y	ND
Lu	ND	Yb	ND
Mg	ND	Zn	ND
Mn	ND	Zr	ND

Key: Very Very Fine Trace = <0.0001%
High = >10%
ND = Not Detected

Physical and Mechanical

Property	*Unit*	*Value*
Apparent Density	g/cc	2.15
Gas Permeability (Helium)	cm^2/sec	2×10^{-11}
Tensile Strength		
"a" direction at RT	MPa (Psi)	41 (6,000)
"a" direction at 2200°C	MPa (Psi)	103 (15,000)
Compressive Strength		
"a" direction at RT	MPa (Psi)	234 (34,000)
Torsional Shear Strength		
RT	MPa (Psi)	10 (1,500)
1500°C	MPa (Psi)	14 (2,000)
Flexural Strength		
"a" direction at RT	MPa (Psi)	83 (12,000)
Young's Modulus		
"a" direction at RT	GPa (Psi)	22 (3×10^6)
Poisson's Ratio		
"a" direction at RT		0.25

Thermal

Property	*Unit*	*Value*
Conductivity		
"a" direction at RT	cal • cm/sec • cm^2 • °C	0.15
"a" direction at 800°C	cal • cm/sec • cm^2 • °C	0.15
"c" direction at RT	cal • cm/sec • cm^2 • °C	0.0037
"c" direction at 800°C	cal • cm/sec • cm^2 • °C	0.007
Total Expansion (Coefficient of Thermal Expansion)		
"a" direction at 260°C	mm/mm • °C	−0.0005 (-1.92×10^{-6})
"a" direction at 1100°C	mm/mm • °C	0.0017 (2.6×10^{-6})
"c" direction at 1100°C (linear)	mm/mm • °C	0.040 (36×10^{-6})
Specific Heat at RT	cal/g-°C	0.24
Thermal Shock Resistance		
2000°C into water		No Damage
Spectral Emissivity at $\lambda = 0.65\mu$		
at 1000°C	$\epsilon\lambda$	0.435
at 1400°C	$\epsilon\lambda$	0.525

Electrical

Property	Unit	Value
Resistivity		
"a" direction at 1000°C	ohm-cm	3×10^7
"a" direction at 1800°C	ohm-cm	6×10^5
"c" direction at 1000°C	ohm-cm	3×10^9
"c" direction at 1500°C	ohm-cm	3×10^5
Dielectric Strength at RT		
("c" direction)	d.c. Volts/mm	2×10^5
Loss Tangent, tan δ		
"a" direction (100 Hz to		
1000 G Hz) at RT		1.3×10^{-4}
"a" direction at 1400 °C		3.9×10^{-4}
"c" direction at RT		$<1.0 \times 10^{-4}$
Dielectric Constant at 4 G Hz		
"a" direction at RT		5.12
"a" direction at 1400°C		5.24
"c" direction at RT		3.4

Chemical

Property	Unit	Value
Toxicity		Non Toxic
Total Impurities	ppm	<100
Total Metallic Impurities	ppm	<10
Oxidation Rate,		
standard air at:		
750°C	$mg/cm^2/min$	Negligible
1400°C	$mg/cm^2/min$	0.2
2000°C	$mg/cm^2/min$	11.0
Outgassing		
at 1500°C.		Negligible